

## Chapter 24 - REPRESENTATIVE SANS DATA

SANS data come in many trends and shapes. Most data sets show a forward scattering peak. Some show a peaked behavior at finite  $Q$ . Only a few show a multitude of peaks. The SANS technique is not abundant in peaks like other characterization methods. Representative SANS data are presented here.

### 1. INCREASING FLUCTUATIONS

Increase in SANS intensity is a signature of an increase in density or composition fluctuations. This is observed for systems undergoing phase transition, aggregation or crystallization. SANS is a good monitor of phase separation.

A figure summarizes SANS data taken from a phase separating polymer solution as temperature is increased (Hammouda et al, 2002). The polymer solution is made of 4 % poly(ethylene oxide) of  $M_w = 41,800$  g/mol in d-water. This high- $Q$  signal represents solvent-polymer interactions (though hydrogen bonding in this case). As temperature is increased, hydrogen bonding breaks leading to the onset of a lower critical solution temperature. The upturn at low  $Q$  is due to a clustering effect characterizing most water-soluble systems.

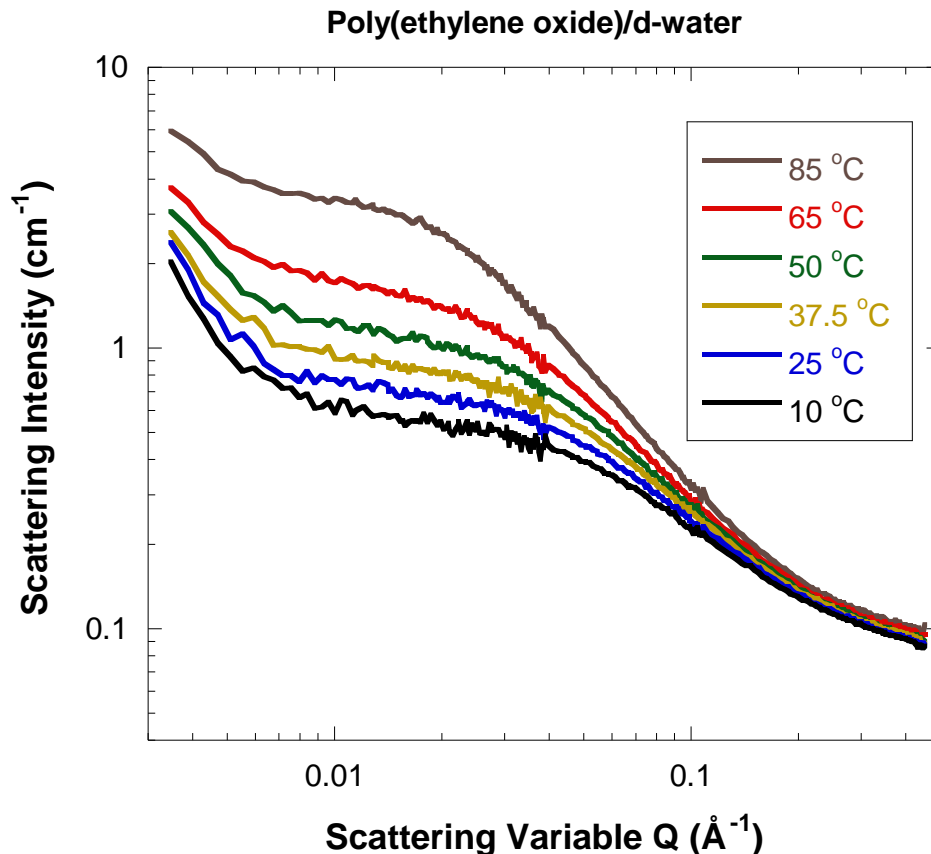


Figure 1: SANS data taken from a 4 % poly(ethylene oxide) solution in d-water. The polymer molecular weight is  $M_w = 41,800$  g/mol.

## 2. ORDERED STRUCTURES

A class of SANS spectra is characterized by a sharp peak. The peak is either due to a well-defined repeat distance (in lamellar systems for example) or due to the correlation hole effect.

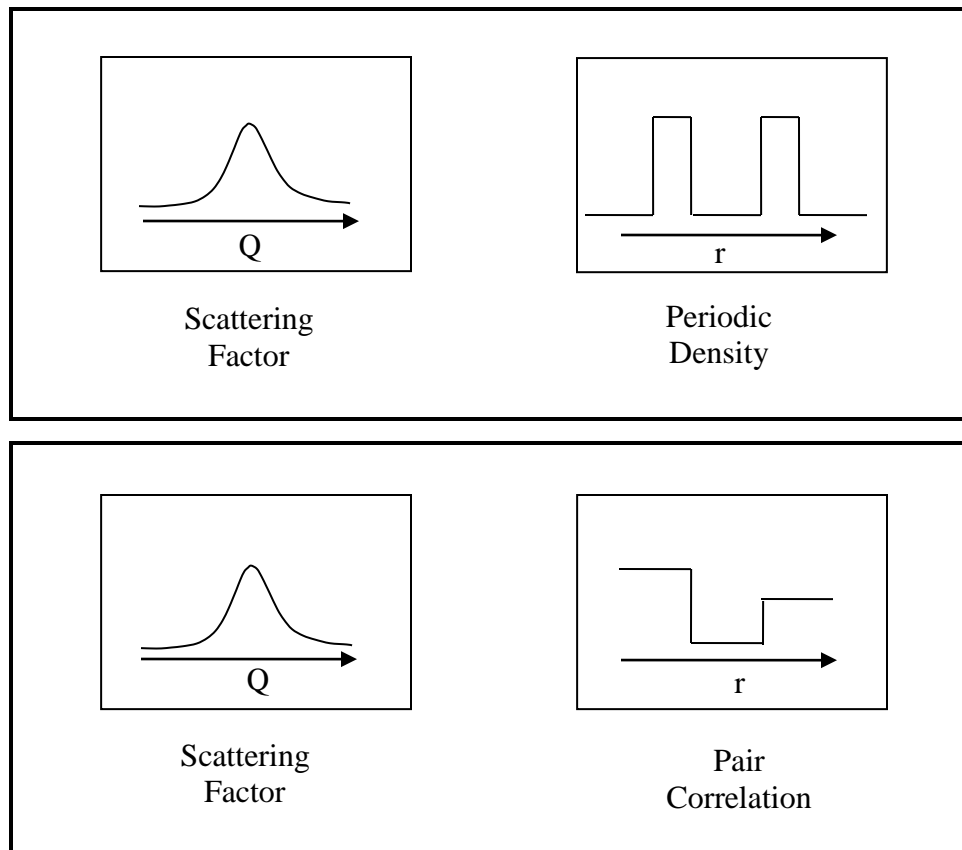


Figure 2: Representation of the two cases that can give a SANS peak.

SANS data from a polystyrene-polyisoprene diblock copolymer are included. The SANS peak is due to the correlation hole. At low-temperatures, the morphology formed is highly ordered (lamellar).

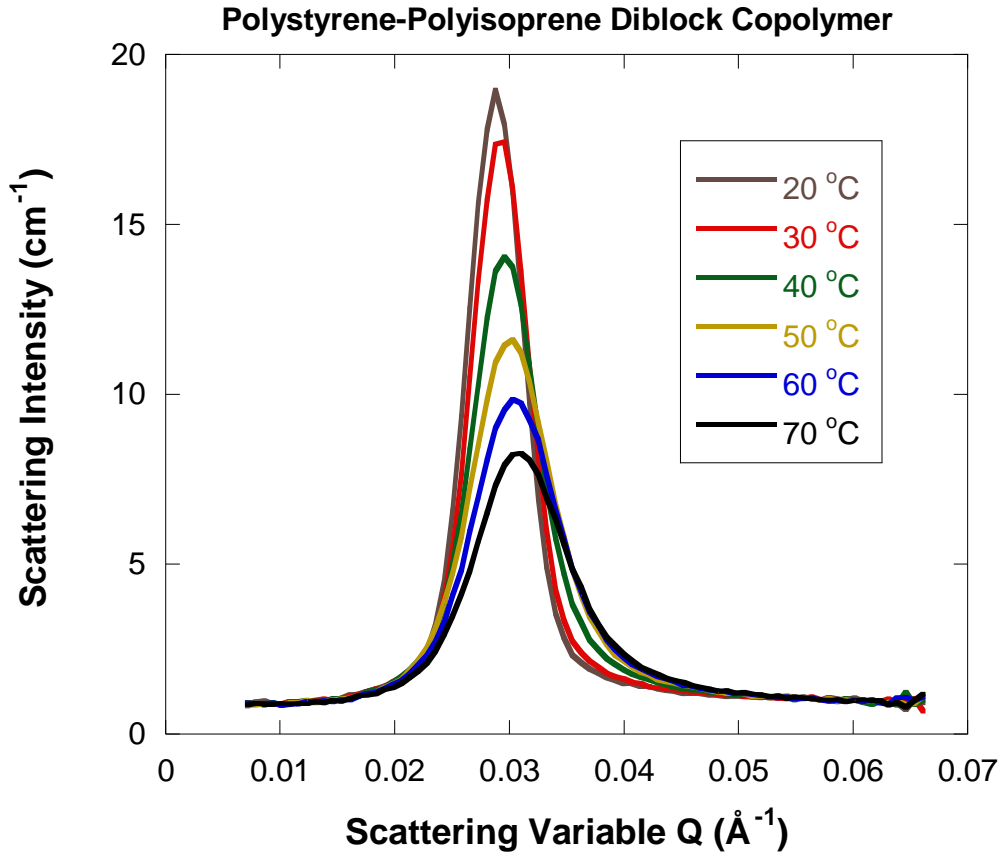


Figure 3: SANS data from a polystyrene-polyisoprene diblock copolymer solution in DOP solvent.

### 3. CONCENTRATED SYSTEMS

Another class of SANS spectra is when an inter-particle peak is formed. This is the case where the inter-particle spacing is comparable to the particle size and is characteristic of “concentrated” systems. The case of a 25 % Pluronic P85 (PEO-PPO-PEO triblock copolymer) micelles in d-water is included. Micelles form above ambient temperature due to the hydrophobic nature of PPO.

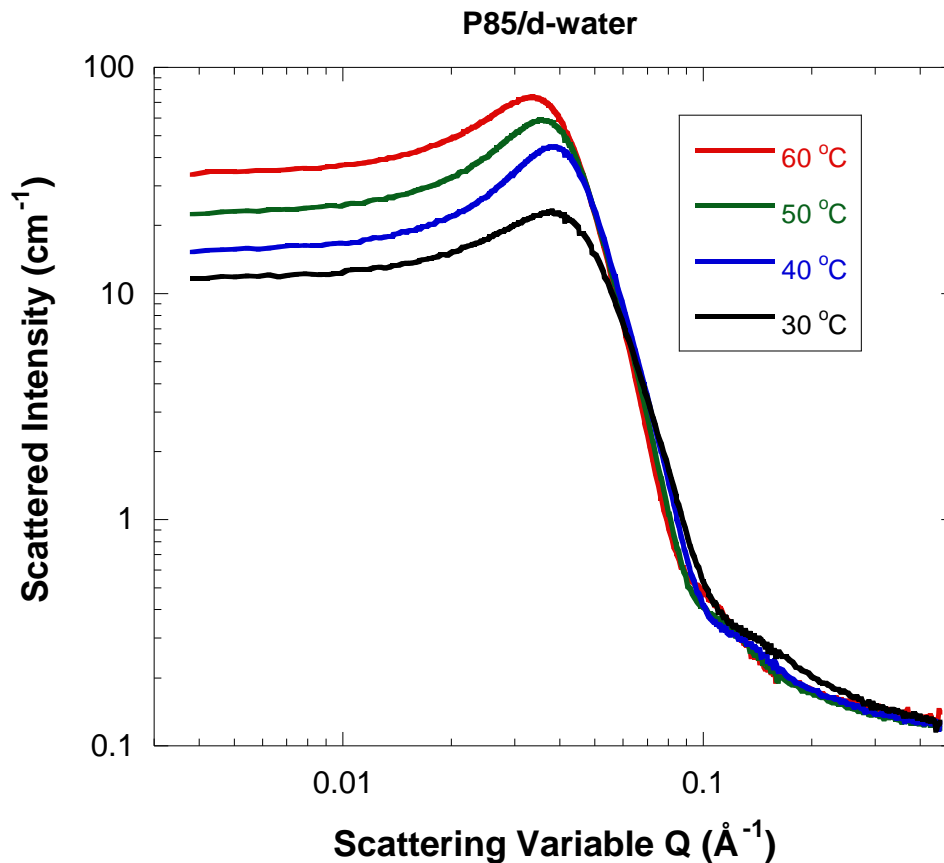


Figure 4: SANS data from **P85 Pluronic micelles**. The inter-particle interaction peak is clearly observed.

#### **4. DILUTE SOLUTION OF MONODISPERSE PARTICLES**

The case of dilute solutions is characterized by scattering from “isolated” particles. A **0.1 % solution of silica particles in d-water** is included here. The higher order peaks are a signature of monodispersity and are limited by instrumental resolution. The fitted sphere radius is  $R = 563 \text{ \AA}$ .

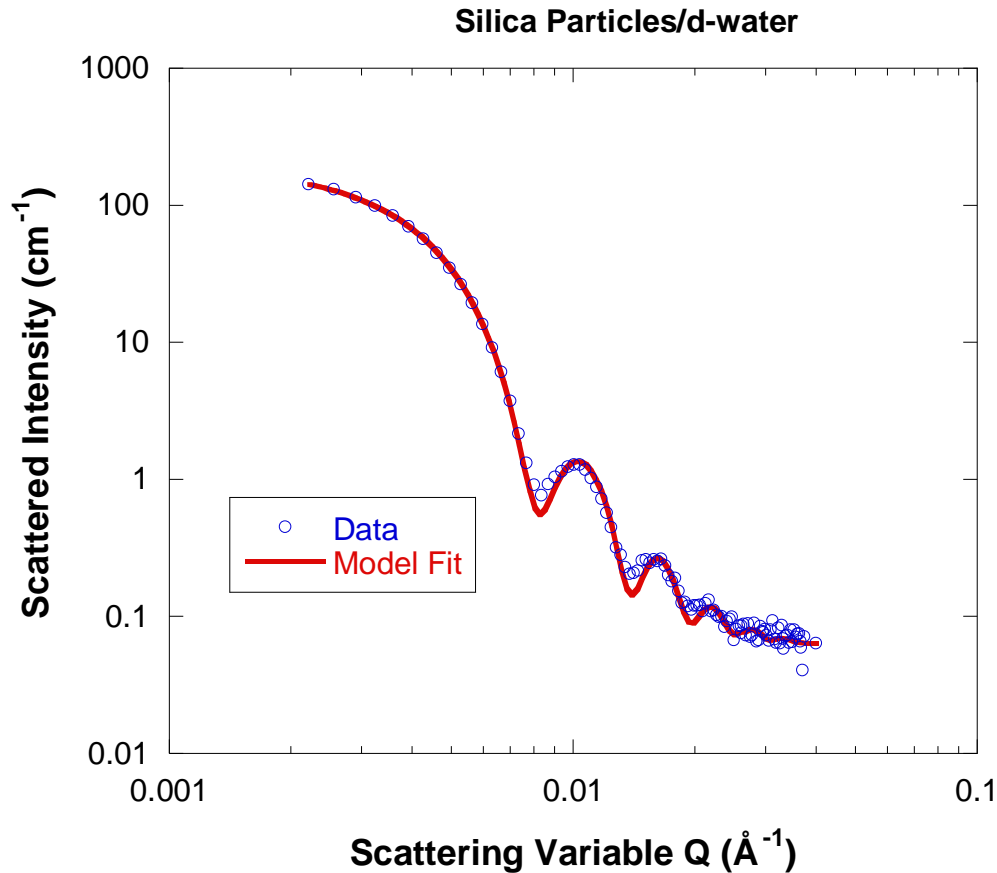


Figure 5: SANS data from a dilute solution of silica particles (0.1 % mass fraction) in d-water and fit to sphere model. The fitted sphere radius is  $R = 563 \text{ \AA}$ .

## REFERENCES

B. Hammouda, D. Ho and S. Kline, "Neutron Scattering from Associating PEO Systems", *Macromolecules* 35, 8578-8585 (2002)

## QUESTIONS

1. Why does scattering increase when a phase transition line is approached?
2. What is the "correlation hole" effect in block copolymers?
3. Why does the block copolymer peak broaden when the mixed-phase region is entered?
4. Why are SANS data from concentrated systems characterized by a peak?
5. What is the origin of the higher order peaks observed in SANS data from monodisperse dilute solution of particles.

## ANSWERS

1. The approach to phase transition conditions is accompanied by composition fluctuations. Likewise molecules attract each other whereas unlike molecules repel each other.
2. Copolymers are formed of blocks that are covalently bonded. Consider, say, a diblock A-B. Around each A block, there is a region where another A block cannot reside because of crowding from B blocks. This region empty of A blocks is referred to as a “correlation hole” effect.
3. The mixed phase (also called disordered phase) region is obtained by dissolving the macrodomain morphology formed in the ordered phase. The SANS peak in the ordered phase is sharp due to the characteristic (lamellar, cylindrical or spherical) morphology. The SANS peak in the disordered phase is due to the correlation hole effect.
4. SANS data from concentrated systems are characterized by a peak because the inter-particle d-spacing becomes comparable to the size of the particles. The SANS peak position characterizes the nearest neighbor inter-distance. It is due to the inter-particle structure factor  $S_I(Q)$ .
5. The single-particle scattering factor for a single spherical particle is given by the spherical Bessel function  $P(Q) = [3j_1(QR)/QR]^2$  where R is the sphere radius and  $j_1(X) = \sin(X)/X - \cos(X)/X$ . This is an oscillatory function with many higher order peaks.